molar energies or enthalpies of vaporization as noted above. High polymers, the other hand, cannot be vaporized (because of their size they have enormous cohesive energies) without decomposition; their solubility parameters must be determined indirectly. Several methods have been employed, most of which use a series of potential solvents with known solubility parameters. In one method the solubility parameter δ_2 for the macromolecule is taken as the midpoint of the range of δ_1s for those liquids that completely dissolve the polymer. If the polymer is not completely miscible, δ_2 is equated to the solubility parameter δ_1 of the liquid in which it has the greatest solubility. In another method the swelling of a lightly cross-linked polymer is measured in the various liquids. The greatest swellings should be found with solvents for which $\delta_1 \approx \delta_2$. The variation of the intrinsic viscosity of the polymer solution with the solubility parameter of the solvent provides yet another method for evaluating δ_2. The viscosity is greatest when $\delta_1 \approx \delta_2$. It is also possible to estimate solubility parameters by summing group contributions (29–31). These and other procedures have been summarized (32). Solubility parameters for large numbers of polymers and solvents have been compiled (30,33).

The solubilities of four polymers in 13 solvents that cover a wide range of solubility parameters have been tabulated (34). This analysis, shown here as Table 2, demonstrates the practical utility of the solubility-parameter method.

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Table 2. Solubilities[a] and Solubility Parameters[b] of Polymer–Solvent Systems[c]

Name	δ_1	Polyisobutylene (δ_2 = 16.2)	Poly(methyl methacrylate) (δ_2 = 18.6)	Poly(vinyl acetate) (δ_2 = 19.2)	Poly(hexamethylene adipamide) (δ_2 = 27.8)
decafluorobutane	10.6	−	−	−	−
neopentane	12.9	+	−	−	−
n-hexane	14.9	+	−	−	−
diethyl ether	15.1	−	−	−	−
cyclohexane	16.8	+	−	−	−
carbon tetrachloride	17.6	+	+	−	−
benzene	18.8	+	+	−	−
chloroform	19.0	+	+	+	−
methyl ethyl ketone	19.0	−	+	+	−
acetone	20.3	−	+	+	−
carbon disulfide	20.5	−	−	−	−
1,4-dioxane	20.5	−	+	+	−
dimethylformamide	24.8	−	+	+	(+)
m-cresol	27.2	−	+	+	+
formic acid	27.6	−	+	−	−
methanol	29.7	−	−	−	−
water	47.9	−	−	−	−

[a] + soluble, − insoluble, (+) soluble at high temperatures only.

[b] The solubility parameters in this table have units of $(J/cm^3)^{1/2}$. To convert to $(cal/cm^3)^{1/2}$, divide by 2.05.

[c] Ref. 34. Courtesy of Plenum Publishing Corp., 1984.

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